APRIL 23, 2013

Verification that FCC Catalysts Cause Pressurization Events at our HTS East Liverpool Facility

Ralph Roper / Heritage Research Group

1. Problem Overview

About two years ago during the months of April and May 2011 a series of at least five pressurization events took place at our HTS East Liverpool facility. Another event took place several months later in December 2011, followed by the most recent event last month (March 3rd, 2013). All of these events took place when bulk loads of spent refinery FCC catalysts, received under a variety of different waste codes and profiles, were being incinerated. The purpose of this document is first to confirm that bulk refinery wastes where the solids fraction is mainly spent FCC catalyst are not compatible with the current HTS incineration process. Guidelines for monitoring and identifying threshold concentrations of FCC catalysts in bulk refinery wastes are also developed and presented.

2. Mechanism of Pressure Events

The pressure events are generally regarded as steam explosions caused by "ash falls." When catalyst wastes are incinerated in bulk, part of the catalyst ends up in the flue gas rather than the slag. The fluidized catalyst adheres to the walls of the secondary combustion chamber (SCC) and/or deposits in dead zones where gas velocity is low. Over a period of a few days the catalyst sinters and ultimately accumulates to the point where it breaks away from the SCC walls and causes an avalanche of hot catalyst to drop into the slag quench pit. Because the catalyst is micro porous with an extremely high internal surface area, the heat is dissipated instantaneously by the water in the quench pit, thereby causing a steam explosion. The composition of the ash and slag recovered from such events, as well as the time and temperature at which it accumulates and sinters inside the SCC are all very consistent with the conditions reported by others (in the coal-fired power plant industry) that lead to an explosive type of ash.

The rate at which catalyst fines accumulate inside the SCC is accelerated by several factors. Feeding this material at high rates sometimes causes a "slag doughnut" to develop about 8-feet down from the front wall. As has been pointed out by Mr. Buchheit, this acts like a dam that interrupts the orderly flow of incoming bulk material and probably causes the incoming catalyst to be fluidized by the flames from the lances. This in turn causes a larger percentage of the catalyst to exit the kiln in the flue gas rather than in the slag. The rapid succession of pressurization events that took place about two years ago is the prime example. Feeding steel drums too rapidly causes a traffic jam inside the kiln which could lead to dispersing the catalyst into the flue gas and more rapid accumulation of catalyst in the SCC.

The severity of an event also depends on several factors and is probably influenced by the depth of the water seal maintained in the quench pit. If the pit is maintained too full, the depth of the water seal will be high thereby enabling a higher pressure to develop inside the SCC during an event.

3. Review of Specific Events

During the April-May 2011 period the problematic material was Sunoco waste No. 96406-12 containing FCC catalyst fines. The chemical profile for this material is listed in Table 1. Among other things, this material seemed to be causing the build-up of slag "doughnuts" in the kiln. Initial loads started on March 9th, 2011 but after at least five pressurization events, the decision was made to terminate this material. No further loads were apparently received after May 10th, 2011.

Table 1 - Waste Stream 96406-12 Chemical Profile

Chemical	CAS No.	Lower Level	Upper Level
ARSENIC	7440-38-2	0	0.048
BENZENE	71-43-2	0.0001	0.0005
CATALYST FINES (FCC)	0	10	30
CHROMIUM	7440-47-3	0	0.0014
LEAD	7439-92-1	0	0.0028
NICKEL	7440-02-0	0	0.0384
SAND, DIRT, GRIT, SCALE, GRAVEL, LIME	0	30	50
VIRGIN PETROLEUM HYDROCARBONS	0	5	20
WATER	7732-18-5	10	20

After a quiet period of several months, nine loads of a similar material from Sunoco were received during the week of December 12th, 2011. The chemical profile of this waste stream (96406-14) indicated it contained "silica alumina catalyst" or, in other words, FCC catalysts (see Table 2). During the course of feeding this material an ash fall incident was experienced on Saturday 17th at 12:05 am that pressurized the system and, like all previous events, blew the water out of the quench pit.

Table 2 - Waste Stream 96406-14 Chemical Profile

Chemical	CAS No.	Lower Level	Upper Level
BENZENE	71-43-2	1	5
PPE	0	0	1
SOLIDS, DIRT,GRIT,SCALE,SILICA ALUMINA CATALYST	0	55	75
VIRGIN PETROLEUM PRODUCTS	0	5	15
WATER	7732-18-5	10	25

Last month, on March 3rd, another ash fall and steam explosion took place while again feeding FCC catalysts. The material came from the Sunoco Marcus Hook plant and was a listed K170 waste. The generator's common name for this material is "Clarified Slurry Oil Storage Tank Bottoms." Five loads were picked up in late December (12/19/2012 - 12/27/2012) and nine loads were pickle up in late February (2/19/2013 - 2/28/2013). Clarified slurry oil is a recycle stream within the catalytic cracking unit from which FCC catalyst has mostly been removed (i.e., "clarified"). The storage tank bottoms are thus residual FCC catalyst fines and the solids content of the most recent material was probably nearly 100% FCC catalyst fines! Indeed, XRF analysis of this material confirmed that to be the case (see Sections 4 and 5 that follow).

Review of the data base for all bulk solids loads received from June 1, 2012 to through March 31, 2013 revealed that, with a minor exception, the Sunoco K170 wastes from the Marcus Hook plant were the only K170 spent catalyst wastes received and that they only came in during the latter parts of Dec 2012 and Feb 2013. The remainder of the 624 bulk loads of refinery wastes from past 10 months caused no such events or issues.

4. Composition of Spent FCC Catalysts

Interpretation of the analytical results first requires an understanding of the general composition of spent FCC catalysts. They are comprised mainly of crystalline alumnosilicates, otherwise referred to as zeolite catalysts. The catalytic activity is strongly influenced by the specific cation(s) occupying the exchange sites within the Si-Al framework. Rare earth ions from a solution containing Lanthanum (La), Cerium (Ce), Neodymium (Nd) and Praseodymium (Pr) are generally exchanged directly onto the zeolite sites. Logically, samples containing spent FCC catalysts would likely contain elevated concentrations of La, Ce, Nd and Pr, whereas others would not.

The heavier fractions of petroleum ("resid") generally contain nickel and vanadium that are notorious poisons to the catalytic activity. Accordingly, FCC catalysts are generally first used on the lighter fractions, from which the spent catalyst is reprocessed (off-site) and resold for resid application. Logically, spent FCC catalyst would come mainly from processing of resid and thus would generally contain elevated concentrations of Nickel and Vanadium.

Manufacturing of FCC catalysts includes addition of a binder material such as silica, aluminum chlorhydrol or peptized alumina. In addition, clay is added to most FCC catalysts as an inert densifier to improve the bulk density of the catalyst. Because the amount of silicon and aluminum in the FCC catalyst product comes from many components, ratios of silica to aluminum have no relevance when it comes to identifying the presence of catalysts in incoming waste streams.

5. Analyses of Ash Samples

Samples of the ash and bulk feed from the March 3rdevent were analyzed and the results were compared to samples of ash and slag from previous events. The results were also compared to samples of quench pit slag/ash previously obtained during normal operations. As will be seen, samples from pressurization events clearly contained large amounts of catalysts whereas those from non-event periods did not.

Samples were analyzed using a variety of methods including X-Ray Fluorescence (XRF), X-Ray Diffraction (XRD) and Thermographic Analysis (TGA). The XRD data for the March 3rd ash indicated a large percentage of the material was a crystalline aluminosilicate compound, as might be expected from FCC catalyst material. The TGA pattern for that sample was very unusual in that an instantaneous weight loss of weight occurred when temperature reached about 700 ^{o}F. Based on review of zeolite literature this was probably from water breaking out of the crystalline aluminosilicate to form a different crystalline compound.

The SRF data were the most revealing. XRF data for quench pit slag/ash during normal non-event periods are summarized in Table 3a; and those for various types of samples from event periods are summarized in Table 3b. The samples in Table 3b included four composites made from the actual slag doughnut from the April 22, 2011 event; and the ash and bulk feed from the most recent March 3rd event. The results in Table 3b clearly show the presence of FCC catalysts. As can be seen by the highlighted columns, the "event" samples all contained elevated concentrations of Ni, La, Ce and Nd whereas the "non-event" samples did not. The XRF results for vanadium and praseodymium were too low to serve as indicators for the presence of FCC catalysts.

Table 3a - SRF Analyses of Quench Pit Slag / Ash During Normal Operation

Sample Date/Time	Description	Ca	Si	Al	Ni	V	La	Ce	Nd	Pr	Mg	Fe
8/21/12 10:40	Slag from quench pit	6.4	7.1	4.5	0.039	0.037	bdl	bdl	bdl	bdl	2.5	7.8
8/22/12 9:45	Slag from quench pit	25.6	0.2	0.0	0.001	bdl	bdl	bdl	bdl	bdl	0.1	0.0
8/23/12 9:20	Slag from quench pit	10.4	12.9	4.1	0.037	0.049	0.0257	bdl	bdl	bdl	2.2	9.3
8/24/12 9:30	Slag from quench pit	5.5	16.3	3.0	0.043	0.030	bdl	bdl	bdl	bdl	2.6	4.4
8/27/12 10:00	Slag from quench pit	7.3	18.4	2.1	0.040	0.039	bdl	bdl	bdl	bdl	1.1	5.2
8/28/12 13:30	Slag from quench pit	15.5	7.7	1.5	0.032	0.048	bdl	bdl	bdl	bdl	0.9	8.4
9/25/2012	Slag from quench pit	10.2	12.4	5.5	0.140	0.045	0.0348	bdl	bdl	bdl	1.9	8.5
10/9/12 13:00	Slag from quench pit	5.5	14.4	4.2	0.028	0.017	0.064	0.009	bdl	bdl	0.9	16.7
10/9/12 15:00	Slag from quench pit	6.1	14.0	4.2	0.108	0.019	0.054	bdl	bdl	bdl	1.2	18.4
10/9/12 20:00	Slag from quench pit	11.8	9.5	3.5	0.061	0.033	0.058	0.009	bdl	bdl	1.5	15.4
10/10/12 4:00	Slag from quench pit	9.5	12.5	4.1	0.040	0.027	0.040	bdl	bdl	bdl	3.4	12.7
10/10/12 16:00	Slag from quench pit	6.4	15.4	8.7	0.025	0.019	0.018	0.009	bdl	bdl	0.7	5.9
10/10/12 20:00	Slag from quench pit	13.7	8.6	5.1	0.047	0.046	0.043	bdl	bdl	bdl	1.7	9.3
10/11/12 4:00	Slag from quench pit	11.1	10.0	3.5	0.207	0.040	bdl	bdl	bdl	bdl	2.1	9.4
10/11/12 10:00	Slag from quench pit	10.5	11.3	3.2	0.189	0.037	0.033	bdl	bdl	bdl	1.5	14.8
10/11/12 14:00	Slag from quench pit	11.1	12.0	3.3	0.037	0.034	bdl	0.0134	bdl	bdl	1.6	13.3

Table 3b - SRF Analyses of Slag, Ash and Feed During Pressurization Events

Sample Date/Time	Description	Ca	Si	Al	Ni	V	La	Ce	Nd	Pr	Mg	Fe
4/12/2011	slag doughnut comp-1	1.9	20.6	19.3	0.382	0.072	2.630	0.192	0.068	bdl	0.9	2.8
4/12/2011	slag doughnut comp-2	1.6	21.5	19.3	0.352	0.073	2.530	0.180	0.069	bdl	0.8	2.3
4/12/2011	slag dougtnut comp-3	2.7	22.3	15.7	0.275	0.062	1.870	0.137	0.050	bdl	1.2	4.8
4/12/2011	slag dougtnut comp-4	2.1	20.6	13.8	0.304	0.061	1.790	0.130	0.044	bdl	1.4	4.1
3/3/2013	Quench Pit Ash	16.3	11.4	4.9	1.570	0.045	0.304	0.059	0.021	bdl	2.1	8.0
3/4/2013	Bulk Feed 3/4/2013	1.5	11.8	5.7	0.284	0.065	0.222	0.042	0.025	bdl	0.6	29.9

5. Recommendations

On the basis of the foregoing, bulk loads of refinery wastes whose solids are comprised mainly of FCC catalysts must no longer be accepted regardless of how the generator characterizes them. These include

- K170 listed wastes, including "Clarified Slurry Oil Tank Bottoms"
- Bulk wastes containing large percentages of FCC Catalyst fines, otherwise referred to as silica alumina catalysts or zeolite catalysts.

Should uncertainty arise as to whether a candidate refinery waste might contain problematic levels of spent catalysts it is suggested that XRF analyses be performed on the samples and the results compared to those in Tables 3a and 3b above. As would be expected, high concentrations of silicon and aluminum in combination with elevated concentrations of nickel, lanthanum, cerium and neodymium are good indicators of the presence of spent FCC catalysts. The results in Tables 3a and 3b can be used as guidelines.

The XRF methodology and device for monitoring such materials will be addressed in a separate memo. Hopefully an existing device previously used at PIZO can be adapted for this application.